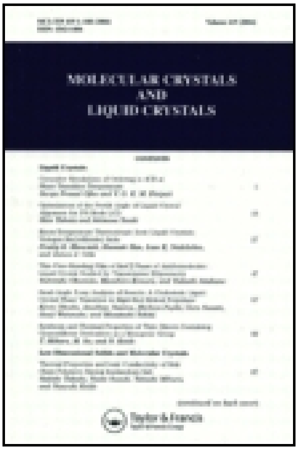

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Dynamic light scattering in nematic liquid crystals in confined geometries

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With photon correlation spectroscopy we have studied dynamical behavior in several systems of nematic liquid crystals embedded in host matrices, i.e., polymer dispersions of nematic droplets, Nuclepore membranes with cylindrical cavities, and porous silica aerogel. In all cases the dynamics of orientational fluctuations is substantially changed compared to the bulk nematic phase and some new phenomena appear. While due to the confinement no long wavelength modes of the director orientational fluctuations are present in the nematic droplets and cylinders, in the nematic liquid crystal in the aerogel a mode with the correlation length of 1-2 orders of magnitude larger than the average pore size was observed. An additional dynamic process with a nearly logarithmic autocorrelation function extending from millisecond to more than ten seconds is more or less pronounced in all three systems and we attribute it to reorientational diffusion in random potential.

Keywords: confined, nematic liquid crystal, dynamic light scattering

INTRODUCTION

The behavior of confined liquid crystals is interesting for applications as well as for fundamental research. The presence of surface strongly affects the configuration of the order parameter and the dynamic response of liquid crystals and these play important role in many liquid crystal devices. Liquid crystals also exhibit a rich collection of phase transitions, so when embedded in different matrices they are interesting for the fundamental research of phase transitions and critical behavior in confined systems.

A powerful tool to investigate the dynamical behavior of liquid crystals is photon correlation spectroscopy[1,2]. Recently many different confined liquid crystal systems have been investigated by this technique. Mostly attention has focused on the behavior of the liquid crystals embedded in various porous matrices[3-6]. In these systems, besides large surface and confinement, also randomness of the host structure influences the properties of liquid crystals. Bellini *et al.*[4] have studied dynamically scattered light in the nematic and the smectic-A liquid crystal in an aerogel host. They found out very complex dynamical behavior that differs from the bulk. Besides well defined orientational fluctuations of the nematic director within pores of aerogel also a process with a broad distribution of relaxation times is present. We have observed similar behavior in the nematic droplets dispersed in polymer matrix (PDLC).

In this paper we present a study of dynamical behavior of nematic liquid crystal in three different confined geometries using photon correlation spectroscopy. The most simple one is the nematic liquid crystal embedded in well defined cylindrical pores of Nuclepore membranes. In the droplets of the PDLC film the nematic director configuration is more complex, but still much simpler than in our third system, a nematic liquid crystal in porous silica aerogel. Although the systems are quite different there are strong similarities in their dynamical behavior.

The paper is organized as follows. In the next section we will briefly discuss the orientational fluctuations modes in the confined geometries and the light scattering by them. The experimental results and discussion are presented in the third section, and are followed by conclusions.

LIGHT SCATTERING IN NEMATIC LIQUID CRYSTALS

To understand the results of the photon correlation spectroscopy experiments in confined nematic liquid crystals two things must be considered. First, the size of a typical cavity is not large compared to the wavelength of light and that must be considered in the analysis of the scattered light. And secondly, due to the confinement the eigenmode structure of the orientational fluctuations in the nematic liquid crystal changes. Instead of plane waves and continuous spectrum as it is in the case of the bulk nematic liquid crystals, the eigenmodes are standing waves with shape depending on the geometry of the cavity, i.e., sinusoidal standing waves in the rectangular geometry[7], Bessel and Neumann functions in the cylinders[8], spherical Bessel functions in the droplets[9] etc. The allowed values of the wave vectors are discreet and depend on the boundary conditions.

The effect of the finite scattering volume

The light is scattered by the inhomogeneities of the dielectric tensor $\underline{\varepsilon}$. In the dipole far field approximation and for the processes that are slow compared to the frequency of light, the electric field amplitude of the scattered light with the wave vector $\mathbf{k}_f$, and the polarization $\mathbf{f}$ is given by[11]

$$E_s(\mathbf{k}_f, t) = \frac{E_0 k^2}{4\pi R} \int_{V_{scatt}} e^{-i\mathbf{q}\cdot\mathbf{r}} (\mathbf{f} \cdot \underline{\varepsilon}(\mathbf{r}, t) \cdot \mathbf{i}) d^3\mathbf{r}, \qquad (1)$$

where R is the distance between the sample and detector, k the magnitude of the wave vector of the scattered light, and $\mathbf{q} = \mathbf{k}_f - \mathbf{k}_i$ the scattering vector. E_0 is the electric field amplitude, $\mathbf{k}_i$ the wave vector, and $\mathbf{i}$ the polarization of the incident light. When scattering volume V_{scatt} is large compared to the wavelength of light λ, the integral in expression (1) is a Fourier transform of a given component of the dielectric tensor. So in the light scattering experiment at a given scattering vector $\mathbf{q}$ one probes modes with the wave vector equal to the scattering vector. When the scattering volume is comparable to λ, the scattering vector need not match any mode wave vector and several modes contribute to scattering. In rectangular geometry the contribution of the mode with wave vector $\mathbf{q}_n$ is proportional to

$$\prod_{j=x,y,z} \frac{\sin\left(\frac{q_{nj}-q_j}{2}a_j\right)}{\frac{q_{nj}-q_j}{2}a_j}. \tag{2}$$

So clearly, when the scattering vector is smaller than the wave vector of the first mode $\mathbf{q}_0$, the largest contribution to the scattered light comes from this mode. At scattering vectors larger than the wave vector of the first mode, mostly the mode with minimal $|\mathbf{q}_n-\mathbf{q}|$ contributes to scattering. In the case of diffusive hydrodynamic modes the relaxation rates are proportional to $|\mathbf{q}_n|^2$ and, therefore, the dependence of the relaxation rates on the scattering vector is quadratic above the $\mathbf{q} \sim \mathbf{q}_0$, while at smaller scattering vectors the main contribution comes from the first mode and relaxation rate is independent of the scattering vector.

Scattering in the nematic liquid crystal

Thermal orientational fluctuations of the nematic director are also the fluctuations of the optical axis and cause strong scattering of light[2]. The director can be written as the sum of the part that describes its configuration $\mathbf{n}_0$ and fluctuating part $\delta\mathbf{n}$ that is much smaller

$$\mathbf{n}(\mathbf{r},t) = \mathbf{n}_0 + \delta\mathbf{n}. \tag{3}$$

When the configuration of the director is homogeneous light is scattered only by the orientational fluctuations $\delta\mathbf{n}$. In one elastic constant approximation the eigenmodes and the relaxation rates of the fluctuations can be calculated from the diffusion equation[2]. In the absence of external fields their relaxation rates are given by

$$\frac{1}{\tau} \approx \frac{K}{\eta}\mathbf{q}_n^2 \tag{4}$$

where K is the elastic constant and η the effective viscosity. The wave vectors of the modes $\mathbf{q}_n$ are determined by the boundary conditions. In the most simple one dimensional confined system, i.e., thin nematic cell, the eigenmodes become standing plane waves. In the case of strong anchoring, i.e., the fluctuating part of the director equals to zero at the boundary, the wave vectors are simply determined by the thickness $2a$ of the nematic cell

$$q_n = \frac{(n+1)\pi}{2a}, \tag{5}$$

and, consequently, the relaxation rate of a given mode is proportional to $1/a^2$. In the case of weak anchoring the situation is different. The boundary conditions lead to secular equations x tan(x) = a/ξ for even and tan(x)/x = a/ξ for odd eigenmodes, where x = qa. The extrapolation length ξ = K/W is determined by the anchoring strength W and the elastic constant. In the limit of small a/ξ, the wave vector of the slowest eigenmode is given by

$$q_0 \approx \sqrt{\frac{1}{a\xi}}, \tag{6}$$

and its relaxation rate

$$\frac{1}{\tau} \approx \frac{W}{\eta a} \tag{7}$$

is then completely governed by the interaction between the surface and the liquid crystal.

In most confined systems the configuration of the director $\mathbf{n}_0$ is spatially dependent and therefore scatters light. If there is only one equilibrium configuration of the director, this scattering is static. In the case that more equivalent configurations of the director are possible, the system can jump from one to another and consequently the light is scattered dynamically. This dynamical process happens on much slower times scales than the orientational fluctuations of the director and can be in most cases treated separately. It can be described as a diffusional motion in a random potential, where the random potential comes from the energy barriers the system must overcome to change the configuration. A characteristic feature for such dynamical process is a broad distribution of relaxation times that is reflected in the spectrum of the scattered light as 1/f noise.

EXPERIMENTS AND DISCUSSION

In our experiments we used a standard photon correlation spectroscopy setup. The light source was a He-Ne laser with the wavelength of 632.8 nm. The intensity correlation function was measured using an ALV5000 correlator that enables measurements over a time range of 10^{-8} - 10^{3} seconds. We have measured the normalized intensity correlation function $g^{(2)}(\tau) = \langle I(t)I(t+\tau)\rangle / \langle I(t)\rangle\langle I(t+\tau)\rangle$ of light exiting the sample as a function of the scattering angle, the size of cavities and in the case of the droplets also as a function of applied electric field. Following the selection rules, and to minimize the elastically scattered background, we chose orthogonal polarizations of incident and scattered light.

Polymer dispersed liquid crystals

The polymer dispersed liquid crystal (PDLC) used in our measurements was provided by the Liquid Crystal Institute, Kent State University. A thin film of the PDLC composed of the nematic liquid crystal E7 droplets dispersed in the polymer matrix was placed between two indium-tin-oxide coated glass substrates. We have studied orientational fluctuations of the nematic droplets as a function of the applied electric field and the scattering angle. The frequency of electric field was 44 kHz. In our scattering geometry the scattering vector was perpendicular to the electric field.

A significant difference was observed between the measured intensity correlation functions when the electric field was applied and when it was absent (Fig. 1). In the bulk nematics at a given scattering vector there are two independent orientational modes that decay exponentially[2]. Depending on the choice of the scattering geometry either of them or both can be observed in the dynamic light scattering experiments, each of them as a single exponential contribution to the correlation function. In the PDLC films in the experiments without the external electric field the system exhibits additional slow dynamics to the one observed in the bulk nematics (Fig. 1). With the increasing external electric field the slow component decreases and, finally, disappears in higher fields leaving almost a single exponential correlation function. We explain this slow nonexponential part as due to rotational diffusion of the average droplet orientation in the random potential that is due to the irregular shapes of the droplets. In the external field the droplets tend to orient along the field and the rotational diffusion is suppressed. The details are explained in Ref. 10.

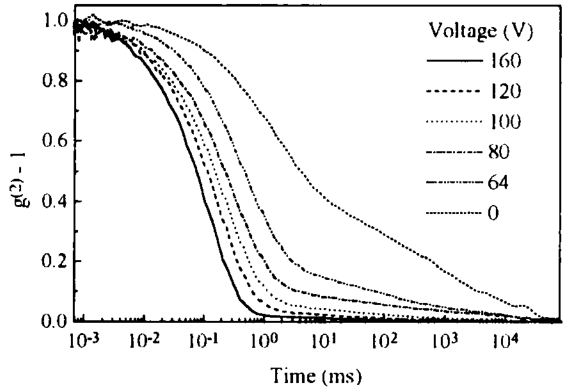

FIGURE 1: Dependence of the normalized correlation function on the applied voltage. The temperature and the scattering angle are 315 K and 30° respectively.

Multiple scattering hinders measurements of the wave vector dependence of the correlation function in the absence of the field. In this case the correlation function does not depend on the scattering vector and since the scattering amplitudes of modes are proportional to $1/q^2$ mostly the lowest mode contributes to the correlation function. The situation is different, however, when the field is applied (Fig. 2).

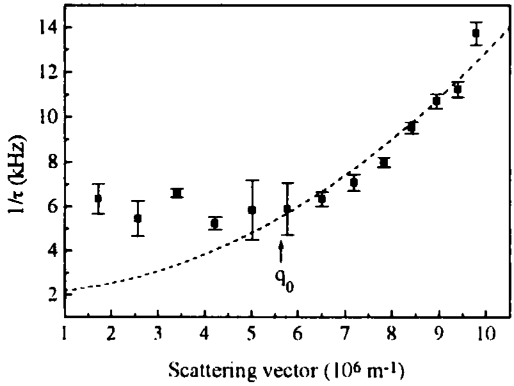

FIGURE 2: Dependence of the relaxation rate of the orientational fluctuations on the scattering vector in the external electric field. The temperature and the amplitude of the applied voltage are 295 K and 160 V respectively.

In fields higher than the threshold field, i.e., the PDLC film is in the transparent state, the inverse relaxation time depends on the scattering vector. Above a certain scattering vector the dependence is strong and can be fitted well with a quadratic function, whereas below this scattering vector the inverse relaxation time has a constant value. As explained in the previous section this limiting scattering vector can be identified as a wave vector of the first, i.e., slowest, mode of the orientational fluctuations within the droplet. This wave vector is determined by the size of the droplet and the boundary conditions. In the case of strong anchoring (expression 5) the size of the droplets is approximately ~ π/q_0, which is in our case ~ 0.5 μm and is in agreement with the droplets' size obtained from the atomic force and the scanning electron microscope images of the polymer matrix of our PDLC sample[11].

Nematic cylinders

The samples were prepared similarly as described in Ref. 12. A piece of polycarbonate Nuclepore membrane was wetted with the liquid crystal 4-

pentyl-4'-cyanobifenyl (5CB) that filled the cylindrical pores of the membrane due to capillary action. The remaining liquid crystal on the surface of the membrane was removed by pressing the membrane between two Whatman filtration papers and then the filled membrane was placed between two glass plates. The configuration of director field in pores of Nuclepore membranes is known to be escaped radial with point defects[12]. The refractive indices of the membranes approximately matches the average refractive index of the 5CB, so the multiple scattering in these samples was negligible.

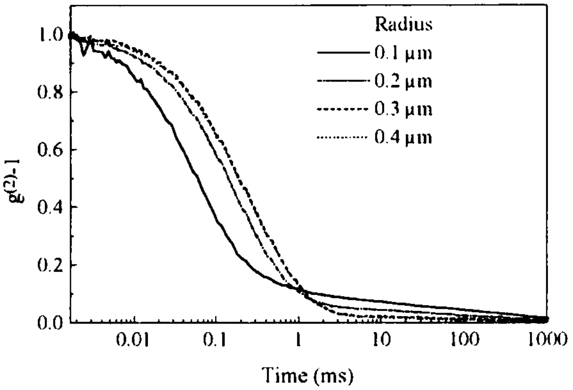

FIGURE 3: Dependence of the normalized correlation function on the radius of the cylindrical pores. The temperature and the scattering vector are 300 K and 5.10^6/m respectively.

The measured intensity correlation function was almost single exponential in the case of the cylinders with radii 0.4 and 0.3 μm, but exhibited additional tail that extended over several time decades for smaller radii (Fig. 3). The exponential relaxation can be attributed to the orientational fluctuations of the nematic director, while the long tail is, similarly as in the nematic droplets, the consequence of the reorientation of the director in a random potential. The origin of the random potential in this system can be in the irregularities of the surface of the pores and of their shape.

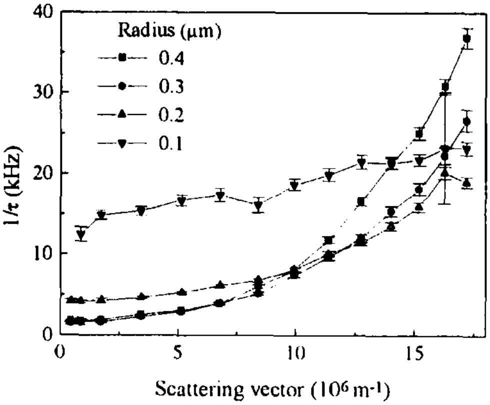

FIGURE 4: Dependence of the relaxation rate of the orientational fluctuations on the scattering vector for different pore sizes. The scattering vector is perpendicular to the axes of the cylindrical pores. The temperature is 295 K.

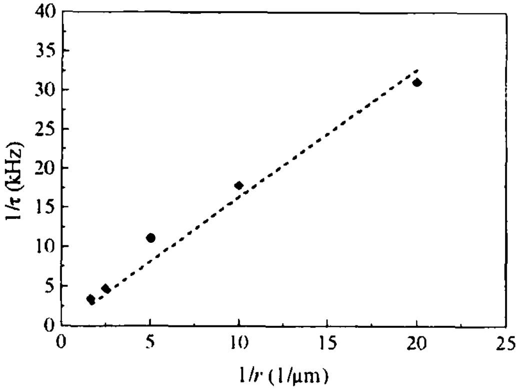

FIGURE 5: Dependence of the relaxation rates of the first mode of the orientational fluctuations on the radius *r* of the cylindrical pores. Dashed line is linear fit. The temperature and the scattering vector are 300 K and 5.10^6/m respectively.

The dependence of the relaxation rate of the director orientational fluctuations on the scattering vector is shown in Fig. 4. As in the nematic droplets also in this system the finite size of the pores limits the maximum wavelength of the fluctuation modes that results in the saturation of the relaxation rate at small scattering vectors. The $1/r$ dependence (Fig. 5) of the relaxation rates of the first modes on the radius indicates the weak anchoring regime (expression (7)). Assuming a value of 0.3 poise for the effective viscosity, we can estimate $W \sim 5.10^{-5}$ J/m^2.

Nematic liquid crystals in a silica aerogel

The silica aerogel used in our measurements has the density of 0.248 g/cm^3 and an average pore size (the pore chord length) of 436Å as was characterized by mercury porosimetry. The pore size is in agreement with the pore sizes determined by small angle X-ray scattering in the aerogels with similar densities[4]. The preparation of aerogels is described in Ref. 13. Thin slices (below 1.5 mm) of the aerogel were cleaved from a larger block and filled with liquid crystal 5CB using capillary action under vacuum. During the filling process the liquid crystal was in the nematic phase. The filled slices were fixed between flat glass plates with the UV cure glue with a refractive index that matched the refractive index of the isotropic 5CB. Only the samples with a good interface between the filled aerogel slices and glue, i.e., the samples completely transparent when the liquid crystal was in the isotropic phase, were used in our measurements to avoid the scattering on the interface.

As in both previous systems also in this case the measured correlation function is nonexponential. Deep in the nematic phase it looks similar to one observed in the PDLC film in the absence of the electric field. Close to the phase transition temperature to the isotropic phase besides the intrapore fluctuations and the long tail, another, slower mode appears (Fig. 6). While the fast mode is independent of the scattering angle, the slow mode shows a quadratic dependence on the scattering vector (Fig. 7). Since no saturation of the relaxation rate at smaller scattering vectors is observed, it can be concluded that the slower fluctuations has a correlation length of the order of the wavelength of light or more, that is, something like 100 average pore sizes. The fast mode can be attributed to the fluctuations of the nematic order parameter within the pores of the aerogel[14].

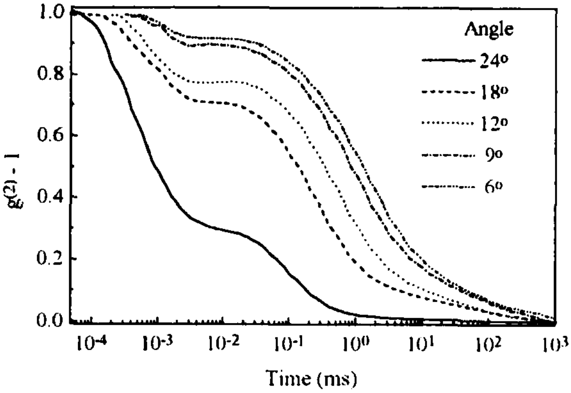

FIGURE 6: Angular dependence of the normalized correlation function 0.7 K below the bulk nematic-isotropic phase transition temperature.

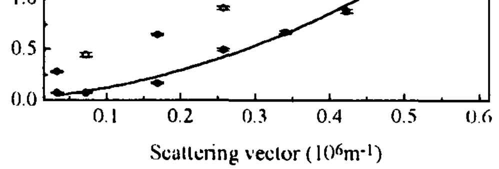

FIGURE 7: Dependence of the relaxation rate of the slower fluctuations on the scattering vector at two different temperatures. For higher-temperature data a quadratic fitting function (line) is also shown.

CONCLUSIONS

In conclusion, the orientational fluctuations of nematic director in confined systems show expected size effect, i.e. the maximal wavelength of the modes is determined by the size of the pores and the boundary conditions. In the nematic liquid crystal embedded in the aerogel besides these interpore fluctuations, another mode was observed that has a correlation length of the order of 100 average pore sizes and that proves the nematic order in different pores is coupled. In all three systems slower dynamical process with a broad distribution of relaxation times was observed. It has been shown[10] that in the PDLC system it can be attributed to the restricted rotational diffusion of the average droplets' orientation, and similar dynamics in the nematic director configuration can also be expected in both other systems.

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